Original Research Paper CHEMISTRY

# Synthesis and Characterization of O-Alkyl ,O-Aryl and O-Cycloalkyl Trithiophosphato Derivatives of Cerium (III) Chloride


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**ABSTRACT**

Chloro cerium (III) trithiophosphates (RO)(S)(P)(S)2CeCl where R = Me ,Et , nPr, iPr, nBu, sBu, iBu , iAm, cyclohexyl, Phenyl ,were prepared in the methanolic solution of CeCl3 and dipotassium salt of trithiophosphate .These newly synthesized derivatives have been characterized by elemental analysis , moleculer weight measurement, I R ,13C ,31P spectral studies. coordination number three is proposed for cerium with discreate trigonal planar geometry.

**KEYWORDS** Ce(III)

**Introduction-**

In the recent years considerable interest have been evinced in the chemistry of metallic moieties bonded with sulfur ligands such as thiolates, dithiolates [1] thio β diketones [2], dithiocarbamates and O-O- alkylene dithiophosphates [3-5] . Dithiophosphinates of lanthanide elements along withthe crystal structure for a few have been reported [6-7]. Synthesis ,characterization and crystal structure of new co-ordination polymers of cerium (III) containing 2-6 pyridine dicarboxylic acid have beenprepared.[8] O-alkyl, O-cycloalkyl and O-aryl trithiophosphato derivatives of Di-propyl Tin (IV) moieties and their adducts with nitrogen donar bases have been synthesized and characterized [9] Complexes of cerium (III) with bis-coumarins:3,3'-benzylidene-bis(4-hydroxy-2H-1-benzopyran-2-one) and bis(4-hydroxy-2-oxo-2H-chromen-3-yl)-(1H-pyrazol-3-yl)-methane were synthesized.[10]Potassium salt of trithiophosphates exist in two isomeric forms ; $[(R0)P(S)S_2]K_2$ and $[(RS)P(O)S_2]K_2$ Organic trithiophosphates esters have been used as defoliants [11] incectesides[11-12] nematocides[12] and inhibitors[13] of steel corrosion. The persusal of literature revealed only two publications on the metallic esters of tri thiophosphoric acids [14-15].The trithiophosphate derivatives of cerium are still unknown. In continuation of our research interest in ligands containing phosphorus and sulfur both, it was thought worthwhile to synthesise a number of compound of the type $(RO)(S)(P)(S)_2CeCl$. In the present communication,we report the synthesis and characterization of a number of chloro cerium(III) trithiophosphates and their reaction with nitrogen donar bases.

**Experimental Procedure**

Dipotassium salt of O-alkyl, O-aryl and O-cycloalkyl trithiophosphates were prepared by the reaction of Phosphorus pentasulfide with corresponding alcohals and triethyl amine in 1:3:3 molar ratio in anhydrous benzene.The reaction mixture was stirred for 30 minute on a water bath. After stirring a methanolic solution potassium hydroxide was added and dipotassium salt was precipitated out . All chemicals were of A.R grade and were used after drying process.

**Measurement-**

IR spectra were recorded in KBr pellets with a Perkin Elmer Model 577 spectrophotometer in the region 4000-200 cm-1. $^1H$ NMR were recorded in water and $DMSOD_6$ using DSS (dimethyl silyl pentyl sulphonate) and TMS (tetra methyl silane) as internal standard . These spectra were recorded on Brucker DRX-300 spectrometer at 75.47 MHz. $^{13}C$ NMR spectra were recorded in water and DMSO using DSS (dimethyl silyl pentyl sulphonate) and TMS (tetra methyl silane) as internal standard. Proton decoupled $^{31}P$ NMRspectra were recorded in water and DMSO using $H_3PO_3$ (ortho phosphoric acid) and as an internal standard. These spectra were recorded on Brucker DRX-300 spectrometer at 121.50MHz. The melting point of the synthesized compound was recorded on B.I.Bornsted electro thermal instrument in a sealed capillary tube Elemental analysis were carried out by standered procedure[16] Carbon, hydrogen and nitrogen were estimated by coleman C,H,N analyzer.

**Resulst and Discussion-**

**$(RO)(S)(P)(S)_2CeCl$**

Chloro cerium(III) trithiophosphates are white colour solids.These complexes are soluble in coordinating solvents as DMSO.Complexes decompose very slowly at room temperature and hygroscopic but remain intact when stored in dry and cooled conditions.

IR spectra-

IR spectra (table1) of chloro cerium(III) trithiophosphate have been measured in the range of 4000-200 $cm^{-1}$ and assignments have been made by comparision with IR spectra of respective Potassium trithiophosphates[17-18].The bands present in the region 1022-1013 and 822-809$cm^{-1}$ have been assigned to β[(P)-O-C] and β[P-O-(C)] stretching vibrations respectively. Strong bands in the region 649-635$cm^{-1}$ is observed due to β[P=S] stretching. Bands due to β[P-S] strech of medium intensity is observed in the region 422-429 $cm^{-1}$, these frequencies are lower in comparison to ligand spectra.This is the direct evidence that coordination occurs with the sulfur.[19] Two new bands also appearsin the complex spectra in the region 349-340 and 360-350 $cm^1$, they are as signed to β[Ce-S] and β[Ce-Cl] respectively. This indicates lowering in symmetry of the ligand because of coordination[20]

**NMR Spectra-**

In $^{31}P$ NMR spectral data (table2) only one signal of phosphorus have been observed which indicates that although two isomers were there in ligand but only one type of ligand isomer is present in compound form Signals are downfield about+19β, ppm and it shows complexation and bidentate nature of the ligand[21]. $^1H$ NMR spectral data are summarized in ( table3). They are in good agreement

with the corresponding alkyl group[22] but more deshielded

compared to the ligand spectra .Percentage of deshielding decreases with the β, β, and β carbons. Some signal obtained in ligand spectra due to $–SCH_3$ at about 2.4 β, ppm is disappearedthus it concluded that only one type of isomer is present in the chloro cerium trithiophosphate complex.Number of hydrogens by integration ratio suggest that there is only one trithiophosphate ligand associated with the cerium.$^{13}C$ NMR spectral data (table3) shows characteristic resonance due to the alkoxy and phenoxy group[21]. The$^{13}C$ resonance for the carbon atom of [P-O-C] group appears as doublet due to coupling with $^{31}P$nuclei. Molecular weight measurement and elemental analysis (table 4) confirm the monomeric nature of the complex .Putting all the facts together coordination number three is proposed for cerium with discreate trigonal planar geometry.The tentative strcture is shown in Fig 1 .

**Aknowledement-**

**Acknowledgement-The author is thankful to CDRI, Lucknow (India).NCL Pune (India) and** USIC, Delhi University (India) for obtaining IR and NMR spectral studies.

**TENTATIVE STRUCTURES**

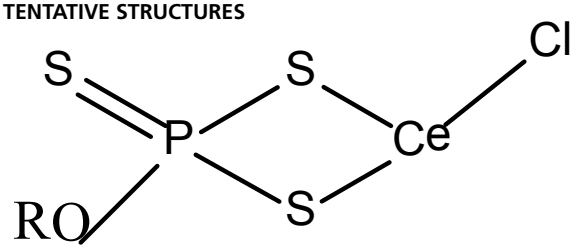


**Fig 1 Structure of $(RO)(S)(P)(S)_2CeCl$**

**Table1: Infra red spectral data for chloro cerium trithiophosphate**

| S.No | Compound | β[(P)-O-C] | β[P-O-(C)] | β [P=S] | β[P-S] | β[Ce-S] | β[Ce-Cl] |
|---|---|---|---|---|---|---|---|
| 1 | $(CH_3O)P(S)(S)_2CeCl$ | 1016(s) | 813(s) | 641(s) | 427(m) | 340(s) | 355(m) |
| 2 | $(C_2H_5O)P(S)(S)_2CeCl$ | 1022(s) | 809(s) | 640(s) | 426(m) | 341(s) | 354(m) |
| 3 | $^{n}(C_3H_7O)P(S)(S)_2CeCl$ | 1020(s) | 819(s) | 635(s) | 422(m) | 342(s) | 359(m) |
| 4 | $^{i}(C_3H_7O)P(S)(S)_2CeCl$ | 1019(s) | 816(s) | 643(s) | 423(m) | 343(s) | 350(m) |
| 5 | $^{n}(C_4H_9O)P(S)(S)_2CeCl$ | 1021(s) | 817(s) | 644(s) | 424(m) | 344(s) | 353(m) |
| 6 | $^{s}(C_4H_9O)P(S)(S)_2CeCl$ | 1020(s) | 815(s) | 646(s) | 426(m) | 346(s) | 360(m) |
| 7 | $^{i}(C_4H_9O)P(S)(S)_2CeCl$ | 1022(s) | 820(s) | 647(s) | 429m) | 349(s) | 358(m) |
| 8 | $^{i}(C_5H_{11}O)P(S)(S)_2CeCl$ | 1015(s) | 822(s) | 643(s) | 424(m) | 344(s) | 357(m) |
| 9 | $(C_6H_{11}O)P(S)(S)_2CeCl$ | 1019(s) | 821(s) | 649(s) | 428(m) | 348(s) | 358(m) |
| 10 | $(C_6H_5O)P(S)(S)_2CeCl$ | 1013(s) | 810(s) | 642(s) | 424(m) | 342(s) | 352(m) |

**Table2 : $^{31}P$ NMR spectral data for chloro cerium trithiophosphate complex**

| S.NO | Compound | $^{31}P$ NMR Data Chemicalshift(βppm) |
|---|---|---|
| 1 | $(CH_3O)P(S)(S)_2CeCl$ | 103.83 |
| 2 | $(C_2H_5O)P(S)(S)_2Ce$ Cl | 104.92 |
| 3 | $^{n}(C_3H_7O)P(S)(S)_2CeCl$ | 104.68 |
| 4 | $^{i}(C_3H_7O)P(S)(S)_2Ce$ Cl | 99.28 |
| 5 | $^{n}(C_4H_9O)P(S)(S)_2CeCl$ | 98.19 |
| 6 | $^{s}(C_4H_9O)P(S)(S)_2CeCl$ | 95.09 |
| 7 | $^{i}(C_4H_9O)P(S)(S)_2Ce$ Cl | 103.65 |
| 8 | $^{i}(C_5H_{11}O)P(S)(S)_2CeCl$ | 104.86 |
| 9 | $(C_6H_{11}O)P(S)(S)_2CeCl$ | 102.74 |
| 10 | $(C_6H_5O)P(S)(S)_2CeCl$ | 101.74 |

**Table3 :$^{13}C$ and $^{1}H$ spectral data for chloro cerium trithiophosphate**

| S.No | Compound | $^{13}C$NMR Data Chemicalshift(β,ppm) | $^{1}H$ NMR Data Chemicalshift(β,ppm) |
|---|---|---|---|
| 1 | $(CH_3O)P(S)(S)_2CeCl$ | 57.39,d,c:$^{2}j_{p-c}$ =19Hz | 4.51(s, 3H,-$OCH_3$) . |
| 2 | $(C_2H_5O)P(S)(S)_2CeCl$ | 65.68,d,c:-$^{2}j_{p-c}$ =22Hz 21.49,$C^2$ | 4.29(q, 2H,-$OCH_2$) 2.4(t,3H,-$CH_3$) |
| 3 | $^{n}(C_3H_7O)P(S)(S)_2CeCl$ | 72.61,d,c:$^{2}j_{p-c}$ =21Hz 28.58, $C^2$ 15.01, $C^3$ | 4.38(t, 2H,-$OCH_2$) 2.16(m,2H,-$CH_2$) 1.16(t,3H,-$CH_3$) |
| 4 | $^{i}(C_3H_7O)P(S)(S)_2CeCl$ | 68.88,d,c:-$^{2}j_{p-c}$ =21Hz 27.86, $C^2$ | 5.19(m,1H,-OCH) 2.38(d,6H,-$CH_3)_2$) |
| 5 | $^{n}(C_4H_9O)P(S)(S)_2CeCl$ | 70.62,d,c:-$^{2}j_{p-c}$ =18Hz 34.53,$C^2$ 15.18 $C^3$ 25.68 $C^4$ | 5.1(t, 2H,-$OCH_2$) 2.1(m,2H,2H,$CH2$,-$CH_2$) 1.1(t,3H,-$CH_3$) |
| 6 | $^{s}(C_4H_9O)P(S)(S)_2CeCl$ | 73.28, d,c:$^{2}j_{p-c}$ =19Hz 43.68 $C^3$ 29.28 $C^4$ 26.31 $C^1$ | 4.7 (d, 1H,-OCH) 1.71(m,2H,-$CH_2$) 1.10(m,6H,-$(CH_3)_2$) |
| 7 | $^{i}(C_4H_9O)P(S)(S)_2CeCl$ | 73.31, d,c:$^{2}j_{p-c}$ =29Hz 33.48 $C^2$ 23.36 $C^3$ | 4.92(t, 2H,-$OCH_2$) 2.21(q, 1H, -CH) 1.31 (d,6H,(-$CH_3)_2$) |
| 8 | $^{i}(C_5H_{11}O)P(S)(S)_2CeCl$ | 64.43,d,c:$^{2}j_{p-c}$ =30Hz 42.31 $C^2$ 28.33 $C^3$ 25.69 $C^4$ | 4.68(t, 2H,-$OCH_2$) 2.33(q, 2H, -$CH_2$) 1.62(m,1H,-CH) 1.03(d,6H,(-$CH_3)_2$) |
| 9 | $(C_6H_{11}O)P(S)(S)_2CeCl$ | 75.71,d,c:-$^{2}j_{p-c}$ =348Hz 36.29 $C^{2,6}$ 28.04 $C^{3,5}$ 31.38 $C^4$ | 5.1(m,1H,-OCH) 1.63-2.38 (m,10H,$(CH_2)_5$) |
| 10 | $(C_6H_5O)P(S)(S)_2CeCl$ | 162.59,d,c:-$^{2}j_{p-c}$ =444Hz 122.86 $C^{2,6}$ 138.50 $C^{3,5}$ 128.71 $C^4$ | 10.3-11.35(m,5H,Arom.) |

**Table 4: Analytical data for chloro cerium trithiophosphate**

| S.No | Compound | Mol.Wt | % Ce | %S | %Cl | %C | %H |
|---|---|---|---|---|---|---|---|
| 1 | $(CH_3O)P(S)(S)_2CeCl$ | 331.67 (333.7788) | 40.98 (41.6173) | 27.64 (28.8208) | 9.69 (10.6217) | 2.63 (3.5984) | 0.81 (0.9058) |
| 2 | $(C_2H_5O)P(S)(S)_2CeCl$ | 346.78 (347.8056) | 39.85 (39.9389) | 26.45 (27.6585) | 9.95 (10.1933) | 5.40 (6.9067) | 1.40 (1.4489) |
| 3 | $^{n}(C_3H_7O)P(S)(S)_2CeCl$ | 360.54 (361.8324) | 37.45 (38.3907) | 25.48 (26.5863) | 9.64 (9.7981) | 9.21 (9.9584) | 1.86 (1.9498) |
| 4 | $^{i}(C_3H_7O)P(S)(S)_2CeCl$ | 360.45 (361.8324) | 37.72 (38.3907) | 25.59 (26.5863) | 9.45 (9.7981) | 9.31 (9.9584) | 1.72 (1.9498) |
| 5 | $^{n}(C_4H_9O)P(S)(S)_2CeCl$ | 374.68 (375.8592) | 36.91 (36.9579) | 24.92 (25.5941) | 8.56 (9.4325) | 11.92 (12.7824) | 2.31 (2.4134) |
| 6 | $^{s}(C_4H_9O)P(S)(S)_2CeCl$ | 374.56 (375.8592) | 36.98 (36.9579) | 24.81 (25.5941) | 8.88 (9.4325) | 11.85 (12.7824) | 2.25 (2.4134) |
| 7 | $^{i}(C_4H_9O)P(S)(S)_2CeCl$ | 374.89 (375.8592) | 36.42 (36.9579) | 24.72 (25.5941) | 8.92 (9.4325) | 11.36 (12.7824) | 2.36 (2.4134) |
| 8 | $^{i}(C_5H_{11}O)P(S)(S)_2CeCl$ | 388.45 (389.886) | 35.01 (35.6283) | 23.95 (24.6733) | 8.72 (9.0931) | 14.35 (15.4032) | 1.94 (2.8443) |
| 9 | $(C_6H_{11}O)P(S)(S)_2CeCl$ | 400.56 (401.897) | 33.98 (34.5635) | 22.01 (23.9359) | 7.95 (8.8214) | 17.35 (17.9314) | 17.01 (2.7586) |
| 10 | $(C_6H_5O)P(S)(S)_2CeCl$ | 394.56 (395.8496) | 34.92 (35.0916) | 22.40 (24.3016) | 8.10 (8.9561) | 17.01 (18.2053) | 17.95 (1.2730) |

Observed (calculated)

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